PILLARED MONTMORILLONITE CATALYSTS FOR COAL LIQUEFACTION

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ABSTRACT

Pillared clays contain large micropores and have considerable potential for catalytic hydrogenation and cleavage of coal macromolecules. Pillared montmorillonite-supported catalysts were prepared by the intercalation of polynuclear hydroxychromium cations and subsequent impregnation of nickel and molybdenum. Infrared and thermogravimetric studies of pyridine-adsorbed catalysts indicated the presence of both Lewis and Brönsted acid sites. Thus, the catalysts have both acidic properties that can aid in hydrocracking and cleavage of carbon–heteroatom bonds as well as hydrogen-activating bimetallic sites. These catalysts were applied to the hydrodesulfurization and liquefaction of coal-derived intermediates. The reactions of model organosulfur compounds and coal liquids were carried out at 300°–400°C for 3 hours in the presence of 1000 psi of molecular hydrogen. Reaction products were analyzed by GC/FT-IR/MS/AED. The catalysts have been found to be very effective in removing sulfur from model compounds as well as liquefaction products.

INTRODUCTION

Catalytic functions required for coal liquefaction are hydrogenation of aromatics and hydrocracking of C–C bonds as well as C–S, C–O, and C–N bonds. Thus, metal or metal sulfide sites activate hydrogen for addition to aromatic rings or for hydrogen transfer reactions, and acidic sites are important for bond cleavage activity in coal liquefaction catalysts. High surface areas for the metal sulfide sites are desired for high activity; this can be achieved by dispersion of the metals on a supporting material with some acidic properties.

Because of their acidic properties, smectite clays have been used as catalysts in petroleum cracking and various other reactions. Unfortunately, they dehydrate and collapse at temperatures above 200°C. New coal liquefaction catalysts being investigated at EERC utilize pillared clays as supports for the metal sulfide sites (1–3). Artok and others used a copper-pillared clay for coal liquefaction (4). In pillared clays, large polyoxymetal cluster cations are exchanged (intercalated) between the negatively charged clay layers in place of the hydrated metal ions. When calcined to drive off the water, the polyoxymetal cations form pillars that maintain the clay layer structure, thus creating large spacings between the layers. These structures are stable to 450° and 500°C. Hypothetically, the micropore volumes will be large enough to accommodate macromolecules of the feedstock to be hydrocracked. Chromia-pillared clays, which have interlayer spacings somewhat larger than those present in alumina-pillared clays used in petroleum refining, have considerable potential for coal liquefaction.

RESULTS AND DISCUSSION

A survey of the catalytic hydrocracking activities of various derivatives of natural montmorillonite clay was conducted. These derivatives included both pillared and unpillared forms of the clay as well as the catalysts obtained by impregnating nickel–molybdenum sulfide on the pillared clay as a support. These tests were carried out in a rocking microreactor (tubing bomb) under 1000 psi of hydrogen at temperatures of 300° to 400°C. Bibenzyl (1,2-diphenylethane), diphenyl sulfide, diphenyl ether, and other hydrocarbon compounds were utilized as substrates to model the structural moieties of the coal, especially the bridging groups believed to link the aromatic clusters. Some of the catalysts were then tested with first-stage coal liquids (low-severity Wyodak liquefaction product), and conversions to distillate materials were determined.

To study the effects of acidic sites present on a clay, the concentration of acidic sites on montmorillonite was maximized by converting the clay to an acid-exchanged form. This form of montmorillonite was prepared by washing the cleaned sodium form of the clay with hydrochloric acid. The reaction of the acid-washed clay (AM) with bibenzyl at 350°C gave a 75% conversion of bibenzyl, whereas a blank hydrogenation reaction of bibenzyl with no clay or catalyst gave only 1% conversion to toluene. The yield of benzene resulting from the clay-catalyzed hydrocracking test was only 34 wt%. The yields of ethylbenzene and toluene were very small (1.9% for each). A two-step reaction of the bibenzyl is believed to occur, producing benzene and ethylbenzene in the first step, and ethylbenzene is further cleaved to benzene and ethane in the second step. Yields of the gas products such as ethane were not measured. Toluene is produced in a different type of reaction. The higher yield of benzene compared to toluene in the montmorillonite reaction indicates that Brönsted acid catalysis (ipso protonation mechanism) is more important in the reaction than Lewis acid catalysis (5, 6). Much of the bibenzyl was

converted to condensation products such as phenylethylbibenzyl. These products are formed from addition reactions (Friedel-Crafts reactions) of the carbonium ion intermediates with bibenzyl or products. The large amounts of condensation products observed in the reaction of bibenzyl with the clay indicate that the selectivity of the acid-washed clay for condensation versus cracking is poor.

Chromia-pillared montmorillonite was prepared with two different concentrations of chromia pillars. The low-concentration chromia-pillared clay (LCPC) gave an 80% conversion of bibenzyl, but as with the acid-washed clay, low yields of benzene (27 wt%), toluene (1 wt%), and ethylbenzene (3 wt%) were obtained from hydrocracking. Condensation products were abundant in the reaction products, indicating poor selectivity for hydrocracking. Results with the clay having a high concentration of chromia pillars (HCPC) gave somewhat higher conversion (93%) and more benzene (47 wt%). Formation of cyclohexanes by single-ring hydrogenation reactions was not observed with either of the chromia-pillared clays or with the unpillared acid-washed clay.

Nickel and molybdenum were impregnated in the high chromia-pillared clay and sulfided to give the active clay-supported catalyst (NMHCPC), and the hydrotreatment reaction with bibenzyl was conducted to determine its effectiveness. A conversion of 91% was achieved at 350°C. This conversion is significantly better than the 64% conversion obtained with the high-chromia-pillared clay support, which did not contain the nickel and molybdenum catalyst. The conversion increased to 99% when the reaction was carried out at 400°C.

The products from the reactions of bibenzyl catalyzed by the NMHCPC were found to be a mixture of aromatics and cycloalkanes. The major products were benzene and ethylbenzene, and the minor products were cyclohexane, methylcyclohexane, and alkylbenzenes. These products resulted from hydrocracking as well as from hydrogenation of the aromatic compounds. In contrast to the reactions carried out with HCPC, the amounts of oligomeric condensation products formed during the reaction with NMHCPC were negligible. From these data, we conclude that the introduction of nickel and molybdenum has moderated the activity of the support so that selectivity for hydrocracking relative to condensation is obtained. The high conversion may be attributed to bimetallic sulfide activation of hydrogen to effect at least partial hydrogenation of the aromatic rings. Activation energies for bond cleavage reactions may be lower in the reduced intermediates. Carbonium ion intermediates are more easily reduced by hydride transfer reactions from the hydrogenated intermediates or dissociated hydrogen on the metal sulfide. Thus, the carbonium ions are rapidly reduced and do not survive long enough to undergo addition reactions to aromatic rings that result in condensation and coking.

Reactions of the LCPC with other alkylbenzenes were investigated to determine if the reactions were consistent with the proposed carbonium ion mechanism. Isopropylbenzene (cumene) reacted very rapidly, giving 100% conversion. Benzene was the major product. The more rapid reaction is expected for a reaction involving cleavage of the aryl–alkyl bond of the *ipso*-protonated ring intermediate to give the secondary isopropyl carbonium ion plus benzene. The reaction with phenyldecane occurred with 81% conversion to give benzene as the major product. A large number of various alkylbenzene and indan products were formed in the reaction as a result of carbonium ion rearrangements and cleavage reactions. Cyclohexanes were not observed in the reaction products.

Although single aromatic rings were not hydrogenated by the clay supports, it was interesting to find out whether multiring aromatic systems could be hydrogenated as they are with other acid catalysts such as zinc chloride. Thus, pyrene was reacted with the chromia-pillared montmorillonite to determine if acid-catalyzed hydrogenation of the multiring systems could be effected. The conversion of pyrene to a hydrogenated pyrene mixture was found to be 15%, which is considerably less than that observed for zinc chloride catalysts. For catalysts containing molybdenum and other transition metals, hydrogenation of multiring systems occurs readily. The reaction with pyrene at 350°C did not result in hydrocracking or rearrangements of the pyrene or hydropyrene rings to phenanthrene or other ring systems.

Reactions of diphenyl sulfide were extensively investigated in order to determine the effects of pillaring and nickel molybdenum sulfide loading on hydrodesulfurization activities. The acid-exchanged form of montmorillonite gave a 99+% conversion at 300°C. The products were benzene and thiophenol in a molar ratio of 9.3:1. The relatively high benzene-to-thiophenol ratio shows that the catalyst is effective in cleaving both carbon–sulfur bonds of the diphenyl sulfide; that is, the thiophenol intermediate is further converted to benzene and hydrogen sulfide. The blank hydrogenation reactions of diphenyl sulfide carried out with no clay or catalyst present resulted in conversions of 1% at 300°C and 10% at 400°C. The excellent conversion obtained with the acid-exchanged clay may be attributed to the high acidity of the catalyst. The anionic aluminosilicate

layers of the clay may also have some ability to stabilize cationic intermediates prior to a reduction step in the hydrodesulfurization mechanism.

The catalytic activity of sodium-exchanged montmorillonite was also tested at 300°C with diphenyl sulfide, and a conversion of only 11 % was obtained. Both benzene and thiophenol were formed (molar ratio of 6.9:1). The sodium-exchanged clay has some residual Brönsted acidity from the polarization of the water of hydration of the sodium cations and the hydroxyl groups of the clay layers.

Our hydrodesulfurization studies were then extended to the chromia-pillared montmorillonites. Hydrogenation of diphenyl sulfide with the LCPC resulted in a conversion of 95% to benzene and thiophenol in equimolar amounts. The high conversion can again be attributed to the high Brönsted acidity of the pillared clay. Catalytic acidic sites may be present on the polyoxychromium cation pillars, since they retain some hydroxyl functionality (7).

Formation of equal moles of benzene and thiophenol in the pillared clay-catalyzed reaction suggests that cleavage of only one carbon–sulfur bond of the diphenyl sulfide occurred. In order to determine if the second carbon–sulfur bond can actually be cleaved in this catalytic system, a reaction of thiophenol was carried out with LCPC under the same conditions used for diphenyl sulfide. Analysis of the reaction products showed 95% conversion of the thiophenol to benzene. These results suggest that during the hydrogenation of diphenyl sulfide, the acidic sites in the clay may be poisoned by the hydrogen sulfide product. Further studies at higher temperatures are in progress to determine whether the deactivation can be reversed.

The HCPC was also tested in the reaction with diphenyl sulfide. This catalyst gave a conversion similar to that obtained with the LCPC, but a much higher molar ratio of benzene to thiophenol (12:1) was found in this test. Thus, the final step of the reaction, which involves hydrogenolysis of the thiophenol, proceeded much more completely with the HCPC catalyst.

Hydrotreating diphenyl sulfide with the NMHCPC catalyst resulted in a 98% conversion. A nearly quantitative amount of benzene was formed with only a trace of thiophenol and a small amount of cylcohexane from reduction of the benzene.

Coal liquefaction tests were carried out with the low-severity product from Wyodak subbituminous coal (LSW) and 1000 psi hydrogen at 400°C in rocking microreactors without added solvent, and the product was distilled to determine the conversion of the nonvolatile portion of the LSW to distillate. Acid-washed clay, pillared clay supports, and NMHCPC catalyst, as well as a commercial silica–alumina-supported Ni-Mo catalyst, gave results paralleling the reactions with the test substrates described above. With a commercial nickel–molybdenum (HDN) catalyst, the conversion to distillate was only 20% under the conditions used. The LSW in the presence of acid-washed montmorillonite gave a conversion of 10%. The LCPC and HCPC with LSW gave very poor conversions (2% and 8% respectively) to distillate. Thus, the supports by themselves are evidently too acidic or too nonselective to be useful for coal liquefaction. But addition of metal sulfides to the support modifies this behavior substantially. A conversion of 29% to distillate was obtained for the NMHCPC catalyst. This is a significant improvement over the conversion obtained with the commercial catalyst. Further testing is required to determine whether the catalysis is actually occurring in the interlayer micropores or simply on the outer surface of the clay. Higher conversions of the LSW to distillate were reported earlier for montmorillonite-supported zinc chloride catalyst (1). Zinc chloride complex catalysts are exceptionally active and efficient in cracking coal, but suffer some disadvantages such as deactivation and emission of hydrogen chloride in the presence of sulfur.

CONCLUSION
Hydrotreatment of first-stage coal liquids and model compounds with a selection of acidic and pillared clays with and without incorporated bimetallic hydrogenation catalysts showed that the combination of support acidity and hydrogen activation catalysis was effective in cleaving C–S and aryl–alkyl bonds and hydrocracking coal materials. Some differences in the activities of the support were noted that depended on the nature and · concentration of oxymetal ion used in pillaring the clay. Further efforts are needed to clearly understand these differences.

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TABLE 1

Catalytic Hydrocracking of Bibenzyl
(1000 psig hydrogen pressure, 350°C, 3 hr, catalyst wt/substrate wt = 0.5)

Catalyst	Conv. %	Yield of Products, wt%
None	1	Toluene (trace)
AM	75	Benzene (34.1) Toluene (1.9) Ethylbenzene (1.9)
LCPC	80	Benzene (27.3) Toluene (1.0) Ethylbenzene (3.4)
HCPC	93	Benzene (47.1) Ethylbenzene (3.6)
NMHCPC	91	1-ring (49.1) 2- and 3-ring (46.8)
NMHCPC*	99	1-ring (76.2) 2- and 3-ring (23.1)

* At 400°C.

TABLE 2

Catalytic Hydrotreating of LSW

Catalyst	Product (%)			
	THF-I	THF-S	Distillate	Actual Distillate
AM	20.0	46.0	28.0	10.0
HDN*	14.3	49.6	35.0	20.0
HCPC	29.4	27.6	26.3	8.0
NMHCPC	6.0	46.0	43.0	28.8

THF-I = Tetrohydrofuran – insoluble
THF-S = Tetrohydrofuran – soluble
HDN* = Commercial Nickel-Molybdenum catalyst